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PLASMA SPRAYING OF WO_3: STRUCTURE CHARACTERIZATION OF THE COATINGS

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ABSTRACT

WO_3 coatings with a thickness of 40 ± 20 μm have been obtained on titanium substrates. Scanning electron microscopy and X-ray diffraction have been used to characterize the WO_3 powders before and after injection in the plasma. The same techniques have also been used to characterize the coatings obtained with various projection conditions. The substoichiometry of plasma sprayed tungsten oxide has been determined by thermogravimetry. It is possible to obtain $WO_{2.99}$ (yellow) or $WO_{2.97}$ (dark-blue) directly by projection. A thermal treatment allows the oxidation of $WO_{2.97}$ to the yellow form. It seems that both colored substoichiometric forms of WO_3 display the same crystalline structure but the yellow form shows the most defined X-ray spectrum. Even if the yellow coating diffractograms and the literature X-ray spectrum for orthorhombic WO_3 are similar, it is not possible to ascertain if plasma sprayed coatings are characterized either by the orthorhombic structure alone or by a mixture of the orthorhombic and monoclinic forms.

I. INTRODUCTION

WO_3 is a semiconducting oxide absorbing in the visible part of the solar spectrum. Since it produces stable photoanodes in aqueous solution, this material was contemplated as a possible candidate for assisted photoelectrolysis of water (1-6). Its electrochromic properties are also well known (7-8). Recently, WO_3 powders and films have also been used as photocatalysts in N_2 reduction to NH_3 (9-10).

Our interest is to study the relation between the photoelectrochemical and photocatalytic properties of WO_3 coatings obtained by plasma spray. This industrial technique, well adapted to the production of large size coatings, has already been used to obtain photoanodes with materials like TiO_2 and Fe_2O_3 (11-13). In the present work, the WO_3 projection conditions will be defined and the WO_3 powders and coatings will be characterized by SEM, thermogravimetry and X-ray diffraction.

II. EXPERIMENTAL DETAILS

WO_3 powder (99% pure, from Atlantic Equipment Engineers) has been separated into four fractions, according to the particle diameters: 1-10 μm, 10-38 μm, 38-63 μm and 63-125 μm. These fractions have been projected on titanium (99.9%, Alfa) and alumina (99.8%, Coors) substrates, using an argon-helium (1-1) 30 kW plasma. Before coating, the substrates were carefully degreased with acetone. Titanium substrates were also slightly blasted with alumina grits in order to improve the WO_3 adhesion. X-ray diffractograms were measured using the $K\alpha$ line of Cu.

III. RESULTS

1. Projection of yellow and dark-blue coatings

It is possible to obtain good coatings with all the WO_3 powder fractions if the particles are injected in the end part of the plasma. An injection of the powders in the center of the plasma results in a large vaporization of the material. In that case, satisfactory coatings can only be obtained by using particles having a size larger than 38 μm.

The coatings obtained on titanium are yellow or dark-blue depending upon the deposition parameters. By using a 5.0 cm projection distance, the titanium substrates reach 560-600°C during plasma spraying and yellow coatings are obtained. Cooling the substrates with an air jet and increasing the projection distance to 7.5 cm results in a dark-blue coating. In that case, the maximum temperature of the substrates reaches 100-120°C.

2. Scanning electron microscopy (SEM) of powders and coatings

The melting of WO_3 powders was verified by plasma spraying particles into water. All the four fractions have a similar behavior. SEM pictures of the 63-125 μm fraction are presented, before (Fig. 1) and after projection into water (Figs 2A and 2B). The transformation of angular shapes to rather rounded ones after plasma spraying indicates that most of the particles are melting during their travel into the plasma. The most striking effect on the particle morphology, of the sudden large increase of temperature in the plasma, is the formation of a highly porous material (Fig. 2B).

Polished cross-sections of yellow and dark-blue coatings are presented in the central part of Figs 3 and 4A respectively. Contrary to yellow coatings, the dark-blue ones cannot be polished because of the poor cohesion of the films. However, dark blue coatings can be converted into yellow ones by heating the films at 550°C for one hour in an air atmosphere. Figure 4B shows that after this thermal treatment, the cross-section of the resulting yellow film is similar to Fig. 3 where the yellow coating directly resulted from the projection. All the observed coatings have a thickness of 40 ± 20 μm.

3. Substoichiometry determination

The substoichiometry of the yellow and dark-blue plasma sprayed WO_3 on titanium, has been studied by thermogravimetry. After spraying, the coating is removed from the substrate and analyzed in air atmosphere. The curves of relative weight loss, $\Delta g/g$, as a function of the temperature first, show a slight increase, followed by a plateau region, then by a very quick drop above 1200°C. The thermogram shapes are similar for both coatings.

The observed $\Delta g/g$ increase indicates that both plasma sprayed coatings are substoichiometric and correspond to WO_{3-x}. By using the difference between the initial and the plateau values of $\Delta g/g$, where WO_3 is assumed to be stoichiometric, it was found that the yellow and dark-blue coatings correspond to $WO_{2.99}$ and $WO_{2.97}$ respectively. The rapid $\Delta g/g$ decrease above 1200°C could be attributed to the sublimation of WO_3 (14).

4. X-ray diffraction

Fig. 5 shows the diffractogram of the WO_3 powder before projection. The wide lines are characteristic of a poorly crystallized

solid. It is however possible to recognize the typical pattern of the hexagonal WO_3 structure (15,16). The positions and relative intensities of the published lines are reported in Fig. 5. Furthermore, it is possible to have a visual confirmation of the hexagonal crystallographic structure by observing the SEM picture of the powder before projection. Indeed, prisms with a base displaying 120° angles can be seen in Fig. 1.

Figure 6 shows the X-ray diffractogram of the powder projected into water. Again, wide lines are reflecting a poor cristallinity of this dark-blue powder for which SEM pictures were presented in Figs. 2A and B. It is, however, obvious that the hexagonal crystallographic structure of the starting powder was not kept through plasma spraying.

Figures 7 and 8A present the X-ray diffractogram of the yellow and dark-blue coatings, respectively, obtained directly by projection on titanium. Figure 8B corresponds to the diffractogram of the same coating than in Fig. 8A but after a heat treatment at 550°C in ambient air during 1 h. This heat treated film is yellow.

Generally speaking, all the diffraction spectra presented in Figs. 5 to 8 are similar, as far as the general position of the lines (individual or in groups) is concerned. It is also clear that the spectra characterizing all the yellow coatings (Figs. 7, 8B) display a better crystallinity than the dark-blue film diffractograms (Fig. 8A) Some of the lines appearing in the X-ray diffractogram belong to the substrate. They are identified in the figures. These lines are not present in all the spectra because the film thickness may vary from 20 to 60 μm.

IV. DISCUSSION

Stoichiometric WO_3 may exist under many crystallographic structures thermodynamically stable in well defined temperature ranges. By increasing the temperature from cryogenic regions, WO_3, which is first monoclinic, becomes triclinic at -40°C (17). Then, at 17°C, WO_3 becomes again monoclinic. The lattice parameters of the monoclinic form, stable at room temperature, are: a = 7.285 Å, b = 7.517 Å, c = 3.835 Å and β = 90.90° (18,19). By further increasing the temperature, WO_3 becomes orthorhombic at 330°C. The lattice parameters characterizing the latter structure are: a = 7.384 Å, b = 7.512 Å and c = 3.846 Å (20). Finally, orthorhombic WO_3 becomes tetragonal at 740°C (21). Other crystalline forms have also been observed for WO_3. For instance, a cubic structure (22) and an hexagonal one (15,16) are mentioned in the literature. The latter structure was found to be characteristic of the starting WO_3 powders in this work.

On the other hand, it was shown by thermogravimetry that the coatings obtained by plasma spray on titanium substrates, were not stoichiometric. Yellow and dark-blue films corresponded to $WO_{2.99}$ and $WO_{2.97}$ respectively.

It is known that the structure of stoichiometric WO_3 is characterized by lightly distorded octahedra having a central tungsten atom surrounded by six oxygens on the apexes (23). In three dimensions, the structure of stoichiometric WO_3 is such that each octahedron is bounded by each apex to six neighbor octahedra. When WO_3 becomes substoichiometric (WO_{3-X}), it has been demonstrated by microscopy (24) that for X values greater than 0.0001, oxygen is not lost at random in the lattice. On the contrary, crystallographic planes are formed, along which some octahedra are sharing common sides instead of common apexes with their neighbors. The number of octahedra involved in this structural reorganization increases with the value of x.

It seems however, that the crystalline structure of WO_{3-x} remains identical to the one of stoichiometric WO_3 at least up to $x = 0.02$ (25). But from $x > 0.04$, the X-ray diffractogram becomes different (25). For instance, weak intensity lines appear for 2θ values smaller than 22°. Positions and relative intensities of X-ray diffractograms were also reported for $WO_{2.90}$ and $WO_{2.72}$ (18).

The yellow coatings directly obtained by plasma spraying of WO_3 on titanium have a value of $x = 0.01$. Its X-ray diffractogram is therefore equivalent to the diffractogram of stoichiometric WO_3. Furthermore, the dark-blue films also obtained by plasma spraying of WO_3 display a diffractogram similar but less detailed than the diffractogram of $WO_{2.99}$. It seems therefore that $WO_{2.97}$ would still be characterized by the stoichiometric WO_3 structure rather than by the crystallographic structure of $WO_{2.96}$.

Figure 9 presents all the positions and relative intensities of all the characteristic lines for orthorhombic (Fig. 9A) (20) and monoclinic (Fig. 9C) (19) WO_3 for values of $2\theta < 60°$. The relative line heights measured for the yellow coatings directly obtained by plasma sprayed on titanium (Fig. 7) are also presented in Fig. 9B. Values of $2\theta > 60°$ have not been compared because the observed lines in this diffractogram region are wide and quite structureless.

The resolution of the diffractograms obtained for the yellow coatings in Fig. 7, does not allow the complete identification of the crystallographic structure characterizing these projections. Except for the two lines at $2\theta = 50$ and 56°, the relative heights for the diffractogram in Fig. 9B correspond more to the relative intensities of the orthorhombic structure (Fig. 9A) than to the monoclinic one (Fig. 9C). The line positions in Fig. 9B also agree better with the orthorhombic rather than the monoclinic positions. The possibility

remains however that both crystallographic structures (orthorhombic and monoclinic) could be present together in the coatings obtained by plasma spraying of WO_3.

The monoclinic form is the stable structure at room temperature. It would not be surprising, however, to detect a metastable phase in the plasma sprayed coatings since the temperature of the melted particles drops very drastically upon reaching the substrate. This has already been observed for TiO_2 for instance. The coatings obtained by plasma spraying this material are always characterized by the rutile crystallographic structure (26) instead of anatase or brookite which are stabler phases at room temperature (27).

The two kinds of coatings (yellow and dark-blue) directly obtained by plasma spray can be understood in terms of phase diagram and projection conditions. The plasma increases considerably the WO_3 temperature resulting in a loss of oxygen (28). It is only under substoichiometric conditions, which eventually could go as low as $WO_{2.72}$, according to the phase diagram, that the material is able to exist in the liquid phase at temperatures above ≈ 1500°C (29). WO_3 also sublimes very quickly above 1200°C as it was noticed by thermogravimetry.

The morphology changes, affecting the particles which have been submitted to the plasma temperature, are frozen by their projection into water. Figure 2A shows that some melting of the starting powders happened but their porous aspect probably results from the sublimation of the bulk of the particles through an already melted external layer, rather than by oxygen loss by WO_3 to become substoichiometric. Upon cooling, material retraction would happen along the canals open in the melted layer by the stream of bubbles escaping from the subliming center. The combinaison of sublimation and cooling would result in a

porosity like the one seen in Fig. 2B. As a matter of fact, only the small particles are spherical, indicating a complete melting; larger ones keep the memory of their initial shape.

When these particles reach the substrate and coat it, they are very quickly cooled to the substrate temperature. This temperature is 560-600°C or 100-120°C, depending upon the projection conditions. When the substrate temperature is high enough, the reoxidation of nonstoichiometric WO_{3-x} up to $WO_{2.99}$ can occur during the projection. On the other hand, when the temperature is lower, the reoxidation of nonstoichiometric WO_3 yields $WO_{2.97}$ only. The latter coating can be oxidized further by thermal treatment (550°C during 1 h in air atmosphere).

V. CONCLUSION

It is possible to change the substoichiometry of WO_3 coatings by varying the projection conditions. $WO_{2.99}$ (yellow) or $WO_{2.97}$ (dark-blue) can be obtained directly by plasma spraying WO_3 powders on titanium substrates. A thermal treatment at 550°C during 1 h in ambient air allows the further reoxidation of $WO_{2.97}$. It seems that both colored substoichiometric forms of WO_3 display the same crystalline structure but the yellow form shows the most defined X-ray spectrum. Even if the yellow coating diffractograms and the literature X-ray spectrum for orthorhombic are similar, it is not possible to ascertain if plasma sprayed coatings are characterized either by the orthorhombic structure alone or by a mixture of orthorhombic and monoclinic forms.

The photoelectrochemistry and photocatalysis of these coatings will be presented elsewhere (30).

VI. ACKNOWLEDGEMENT

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FIGURES

Fig. 1 : SEM picture of the starting WO_3 powder with a granulometry between 63 and 125 μm.

Fig. 2 : SEM picture of the WO_3 powder of Fig. 1 after projection into water.

Fig. 3 : SEM picture of the polished cross-section of a yellow coatings, directly obtained by plasma spraying WO_3 on titanium.

Fig. 4 : SEM pictures of polished cross-sections of: (A) dark-blue coatings directly obtained by plasma spraying WO_3 on titanium; (B) yellow coatings obtained after thermal treatment of (A).

Fig. 5 : X-ray diffractogram of the starting WO_3 powder and literature positions and relative intensities for hexagonal WO_3.

Fig. 6 : X-ray diffractogram of the WO_3 powder after projection into water.

Fig. 7 : X-ray diffractogram of yellow coatings directly obtained by plasma spraying WO_3 on titanium.

FIg. 8 : X-ray diffractogram of: (A) dark-blue coatings directly obtained by plasma spraying WO_3 on titanium; (B) yellow coatings after thermal treatment of (A).

Fig. 9 : Positions and relative intensities for $2\theta < 60°$ of: (A) orthorhombic WO_3; (B) yellow coatings directly obtained by plasma spraying WO_3 on titanium; (C) monoclinic WO_3.

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Figure 1: SEM picture of the [illegible]

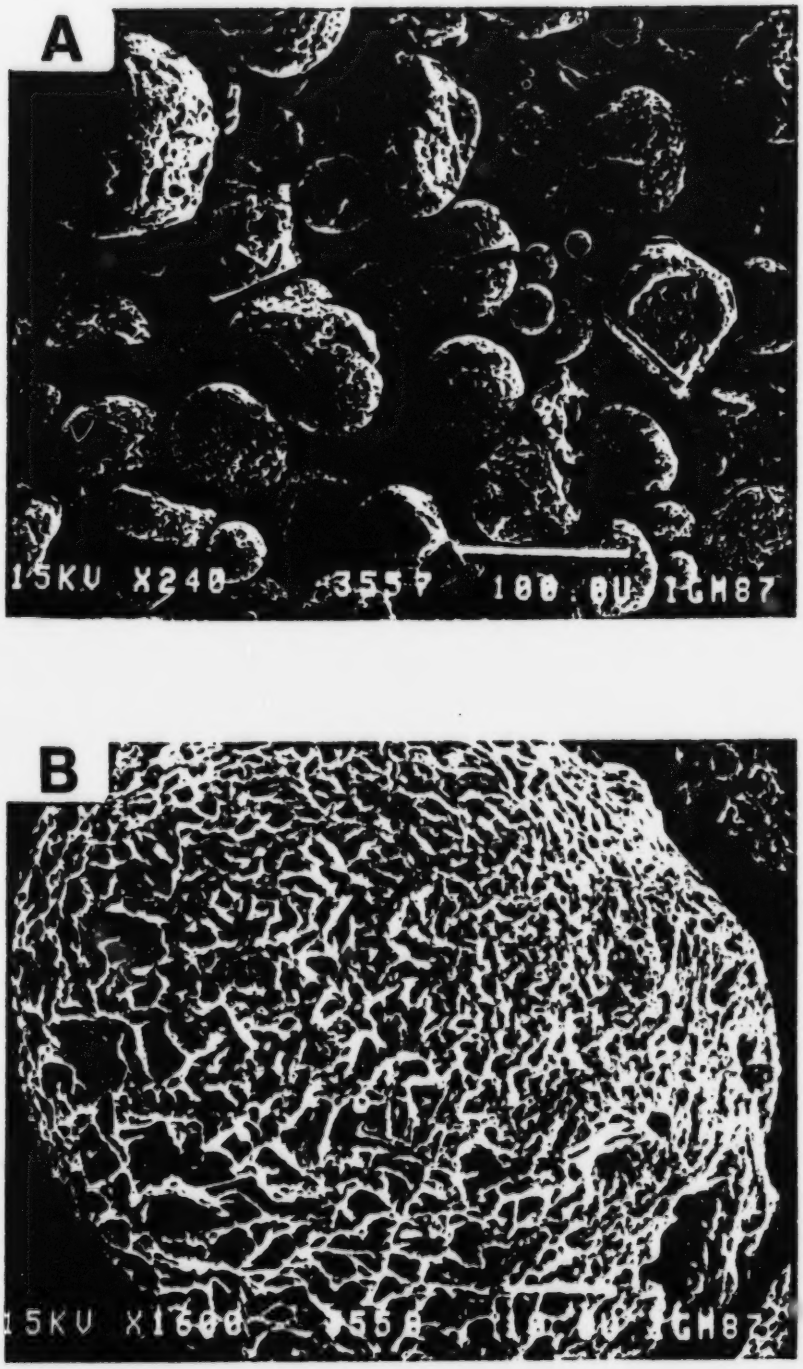

Figure 2: "SEM [illegible] of the WO_3 [illegible]"

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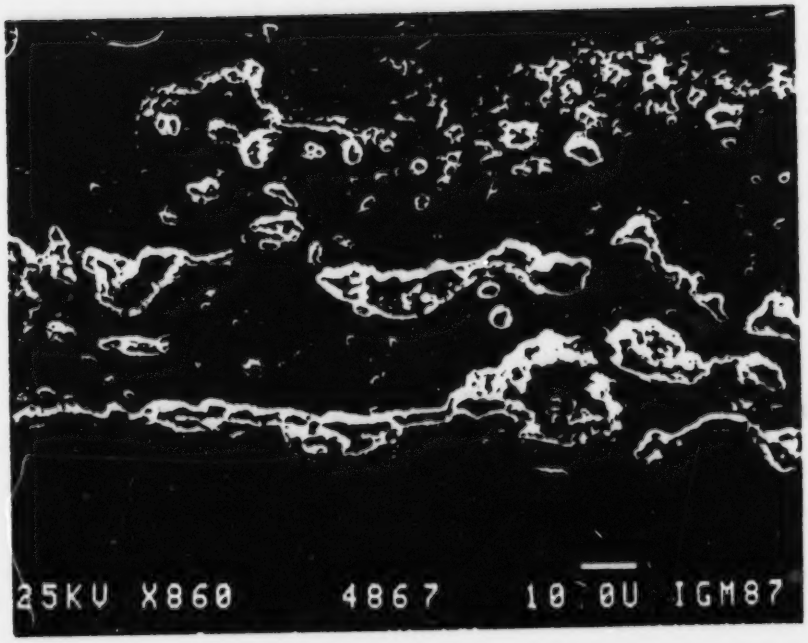

Figure 3: "SEM picture of the polished ..."
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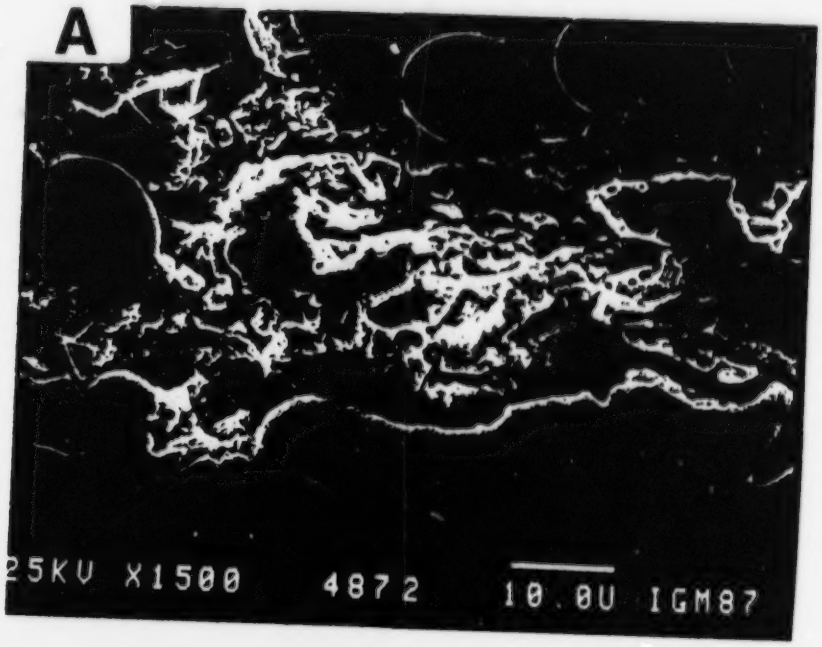

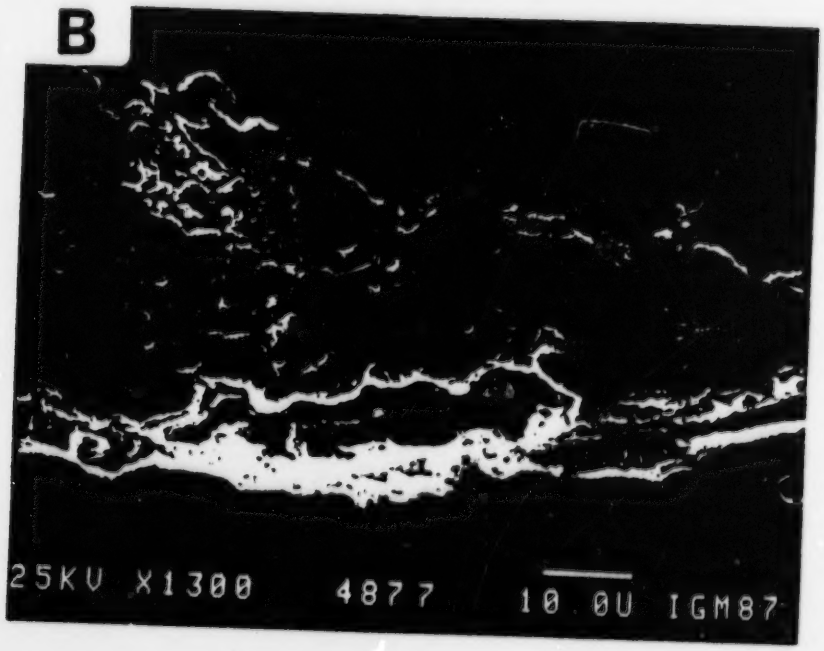

Figure 4: "[illegible] of polished ..." [illegible]

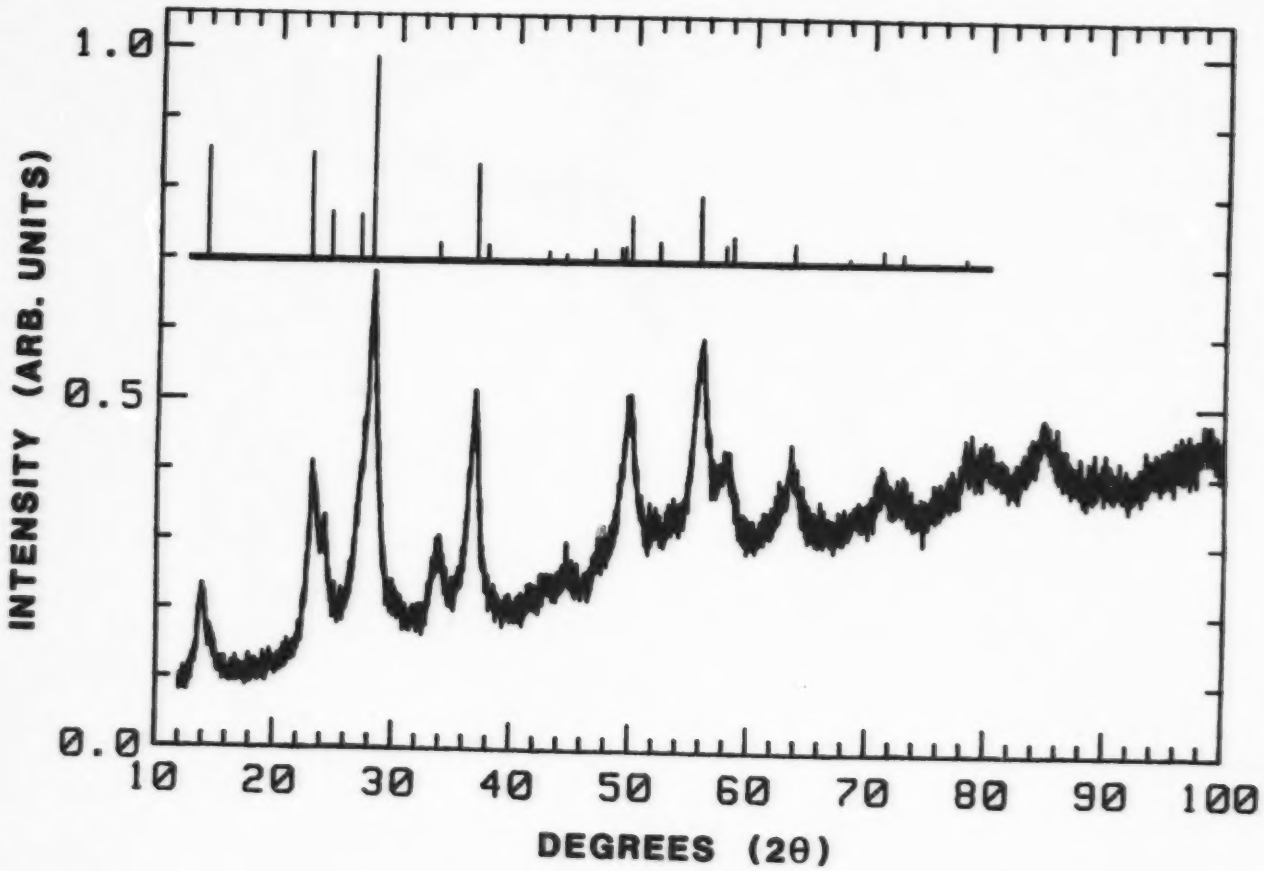
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Fig 5

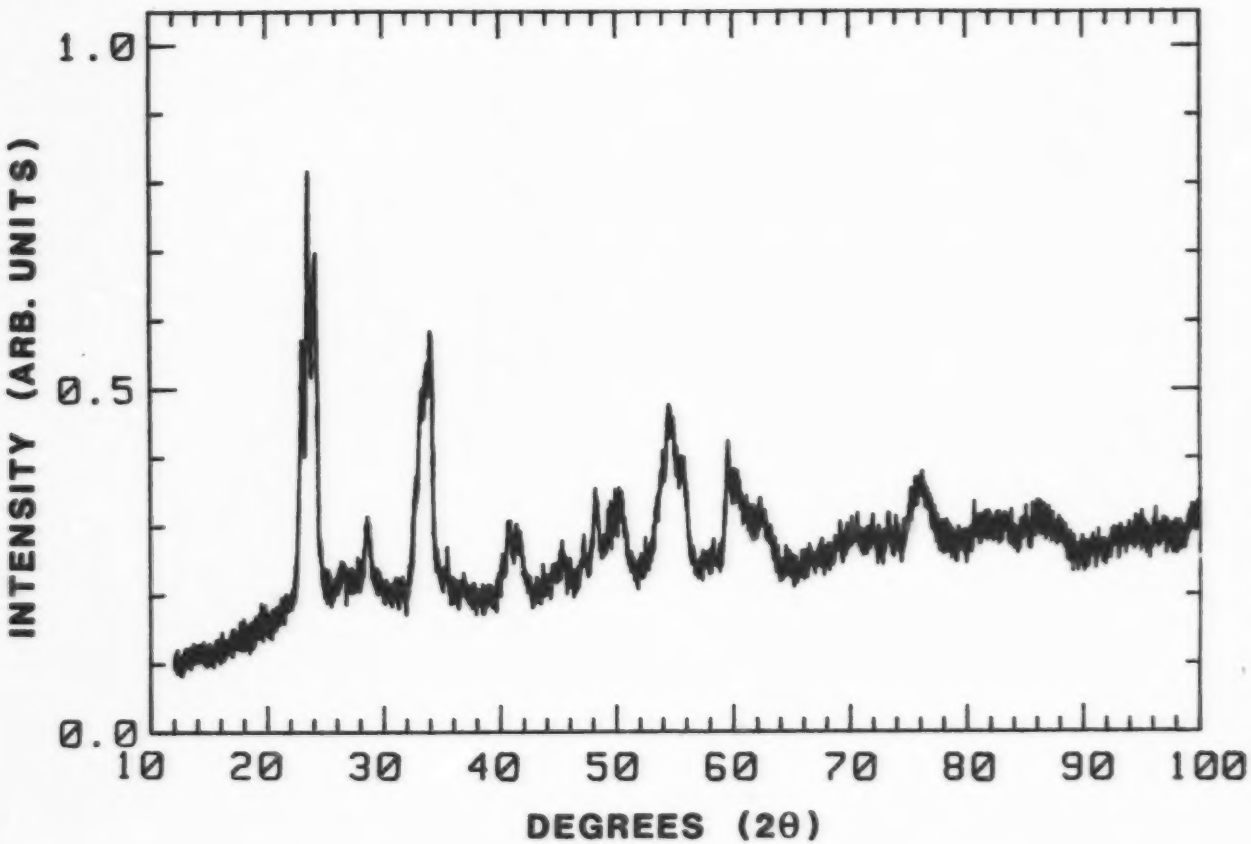
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Fig 6

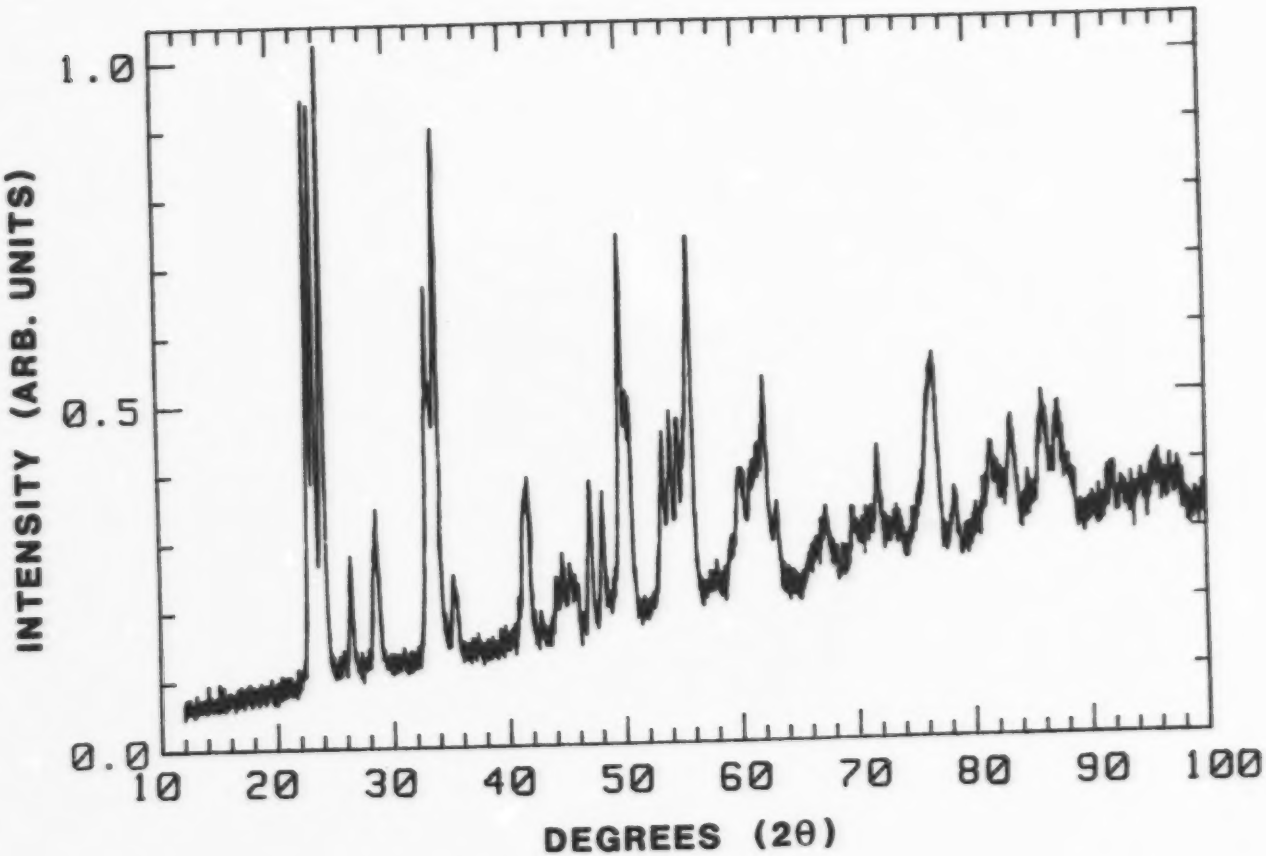
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Fig 7

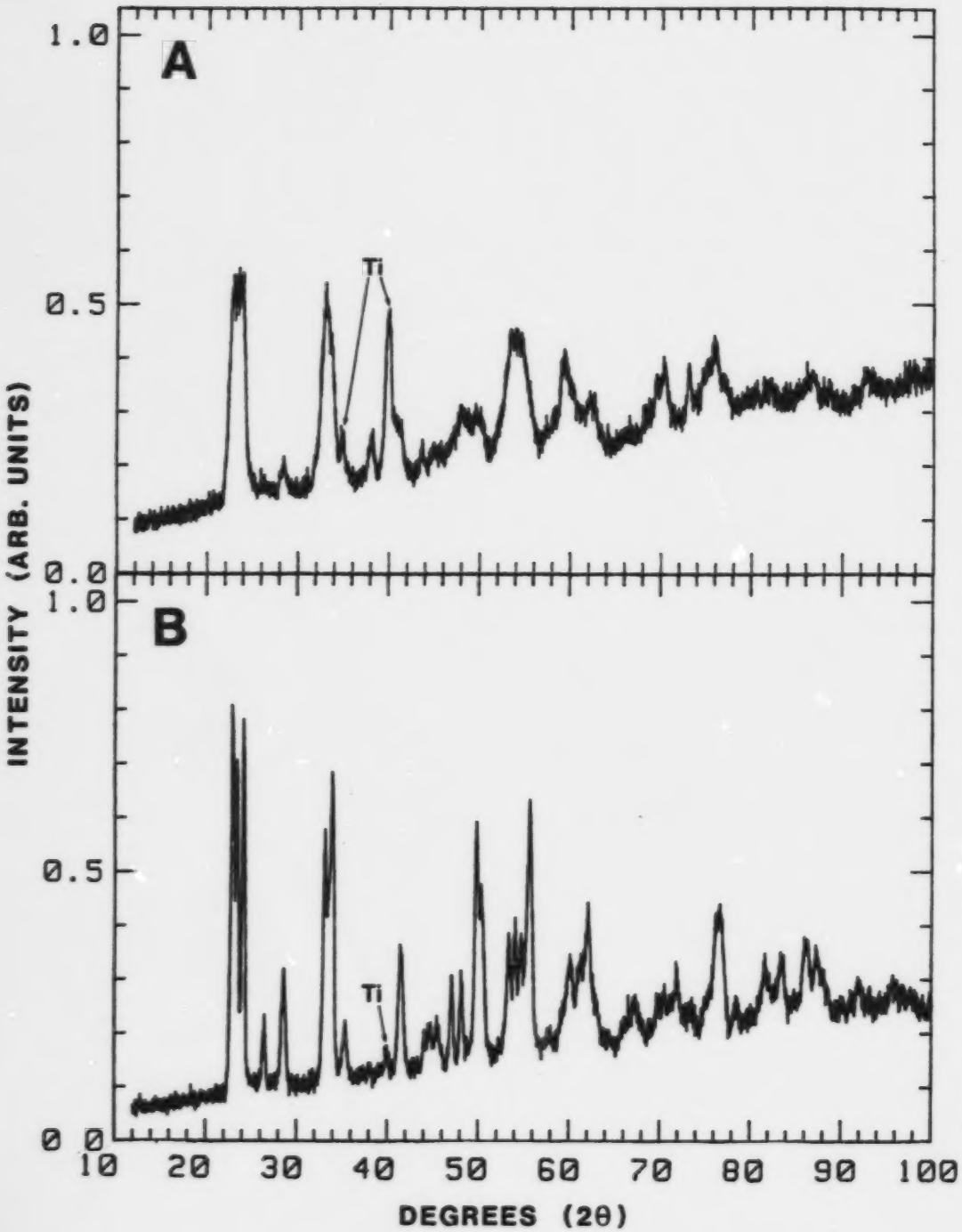
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Fig 8

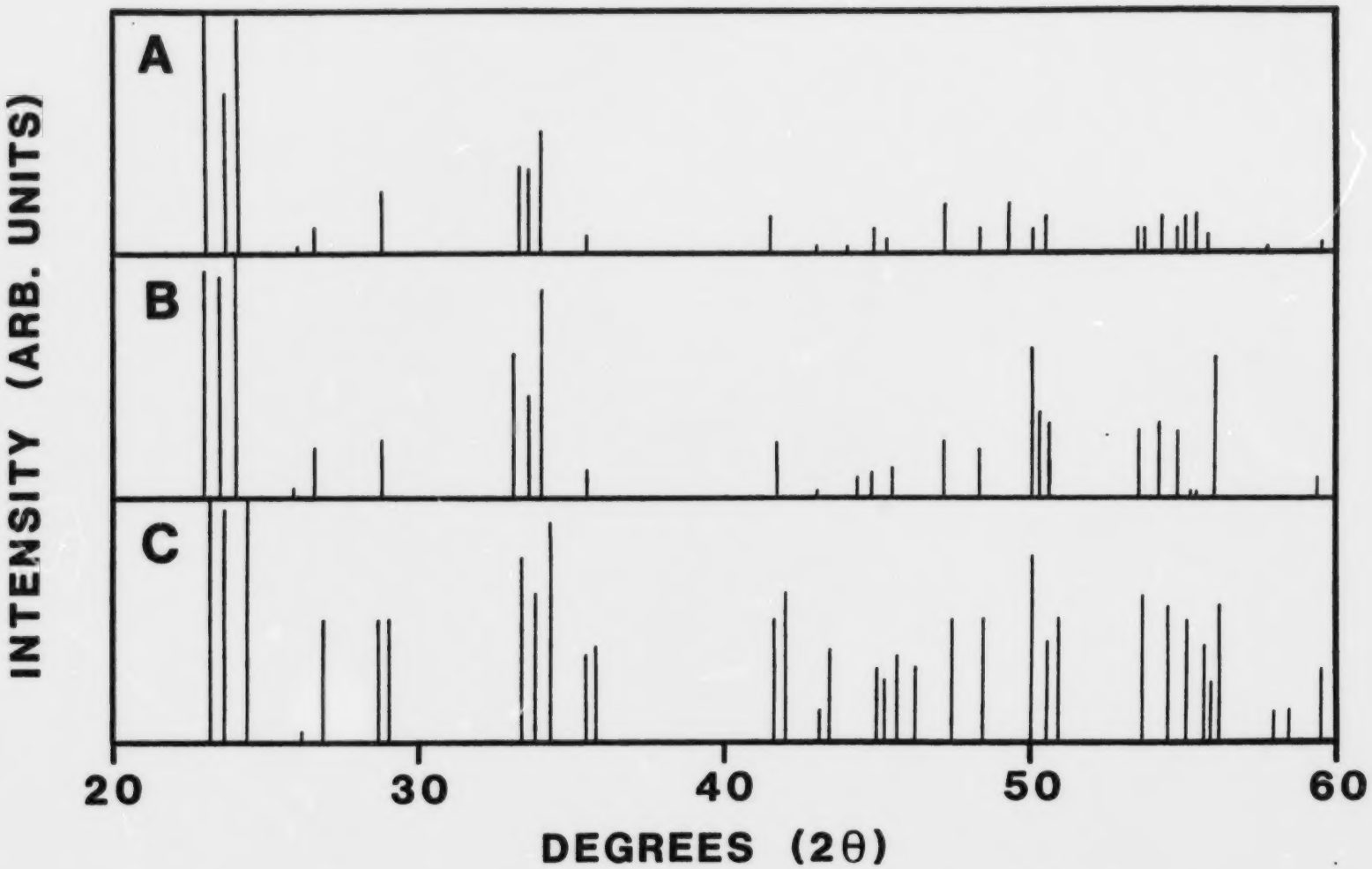

Fig 9